

University of Groningen

Mass Transfer Accompanied With Complex Reversible Chemical Reactions In Gas-Liquid Systems

Swaij, W.P.M. van; Versteeg, G.F.

Published in:
Chemical Engineering Science

DOI:
[10.1016/0009-2509\(92\)85028-A](https://doi.org/10.1016/0009-2509(92)85028-A)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1992

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Swaij, W. P. M. V., & Versteeg, G. F. (1992). Mass Transfer Accompanied With Complex Reversible Chemical Reactions In Gas-Liquid Systems: An Overview. *Chemical Engineering Science*, 47(13), 3181-3195. [https://doi.org/10.1016/0009-2509\(92\)85028-A](https://doi.org/10.1016/0009-2509(92)85028-A)

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Mass Transfer Accompanied With Complex Reversible Chemical Reactions In Gas-Liquid Systems: An Overview

W.P.M. van Swaaij and G.F. Versteeg,
 Twente University of Technology, Department of Chemical Engineering,
 P.O. Box 217, 7500 AE Enschede, The Netherlands

ABSTRACT

In many processes in the chemical industry mass transfer accompanied with reversible, complex chemical reactions in gas-liquid systems are frequently encountered. In point of view of design purposes it is very important that the absorption rates of the transferred reactants can be estimated sufficiently accurate. Moreover, mass transfer phenomena can also affect substantially important process variables like selectivity and yield. Therefore large amounts of research effort has been invested in describing these processes and in the development of models that can be used for the calculation of the mass transfer rates and other parameters.

The description of the absorption of a gas followed by a single first order irreversible reaction is simple and straightforward. For all mass transfer models, e.g. film, penetration and surface renewal respectively, this process can be analytically solved. For other processes however, only for a limited number of special cases analytical solutions are possible and therefore numerical techniques must be used for the description of these phenomena. Besides numerically solved absorption models the mass transfer rates often can be calculated satisfactory accurate by simplifying the actual process by means of approximations and/or linearizations. In this paper an overview will be given of the absorption models that are available for the calculation of the mass transfer rates in gas-liquid systems with (complex) reversible reactions. Both numerically solved and approximated models respectively will be treated and conclusions on the applicability and restrictions will be presented. Also perspectives and white spots will be indicated.

Keywords: absorption, mass transfer, enhancement factor, gas-liquid processes, chemical reaction

1. INTRODUCTION

In the process industry many operations involve the transfer of one or more gaseous components to a liquid phase in which a chemical reaction occurs e.g., the removal of acid components from industrial gases by means of alkanolamine solutions. In order to be able to design the reactors and/or absorbers for the above mentioned processes among others the absorption rates of the gas phase reactants must be calculated. Unfortunately, the estimation of these absorption rates or molar fluxes is not simple and straightforward.

Generally, the molar flux for a gas phase reactant A into a liquid in which a homogeneous reaction takes place, can be described according to eq. (1):

$$J_A = \frac{(C_{A,G} - \frac{C_{A,L}}{m_A})}{\frac{1}{k_G} + \frac{1}{m_A k_L E_A}} \quad \text{mol.m}^{-2}.\text{s}^{-1} \quad (1)$$

and multiplying eq. (1) with the interfacial area the local absorption rate is obtained.

For the determination of the mass transfer coefficients and specifically for k_L , models have been developed for the description of the mass transfer process. The film model in which the mass transfer takes place by stationary molecular diffusion only through a stagnant film as was proposed first by Whitman (1923). It is assumed that a stagnant film of thickness δ exists at the interface, while the bulk of the liquid is well mixed. For the surface renewal models the characteristic parameter is the exposure time of the fluid elements at the interface. Higbie (1935) proposed that all elements have an identical residence time, θ , at the interface, while Danckwerts (1951) introduced a probability of replacement, s . Two-parameter models which are a combination of surface renewal and stagnant film approach have been developed by Dobbins (1956) and Toor and Marchello (1958). They assumed finite dimensions of the fluid elements replaced and their approaches can be regarded as a film-renewal model with two parameters δ and θ .

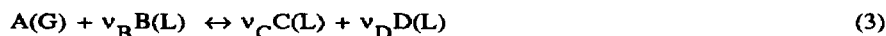
In the present contribution attention will be paid to the calculation of the molar fluxes and especially of the enhancement factor which is defined as:

$$E_A = \left[\frac{J_A \text{ with reaction}}{J_A \text{ without reaction}} \right]_{\text{identical } (C_{A,Li} - C_{A,L0})} \quad (2)$$

2. MASS TRANSFER ACCOMPANIED BY HOMOGENEOUS CHEMICAL REACTIONS

2.1. Introduction.

The problem considered is mass transfer accompanied by a reversible chemical reaction of general order with respect to both reactants and products:



with the following reaction rate equation:

$$R_A = -k_{m,n,p,q} C_{A,L}^m C_{B,L}^n C_{C,L}^p C_{D,L}^q + k_{r,s,t,v} C_{A,L}^r C_{B,L}^s C_{C,L}^t C_{D,L}^v \quad \text{mol.m}^{-3}.\text{s}^{-1} \quad (4)$$

Reactions in gas-liquid systems usually can be expressed sufficient accurately with rate expressions like eq. (4).

For the penetration model the following material balances can be derived:

$$\frac{\partial C_{A,G}}{\partial t} = D_A \frac{\partial^2 C_{A,G}}{\partial x^2} + R_A \quad (5) \quad \frac{\partial C_{B,L}}{\partial t} = D_B \frac{\partial^2 C_{B,L}}{\partial x^2} + \nu_B R_A \quad (6)$$

$$\frac{\partial C_{C,L}}{\partial t} = D_C \frac{\partial^2 C_{C,L}}{\partial x^2} - \nu_C R_A \quad (7) \quad \frac{\partial C_{D,L}}{\partial t} = D_D \frac{\partial^2 C_{D,L}}{\partial x^2} - \nu_D R_A \quad (8)$$

Before solving this set of equations uniquely, one initial condition and two boundary conditions are necessary. As initial condition it is assumed that the system considered is in equilibrium for a given solute loading:

$$t=0 \text{ and } x \geq 0: C_{A,L} = C_{A,L,0}, C_{B,L} = C_{B,L,0}, C_{C,L} = C_{C,L,0} \text{ and } C_{D,L} = C_{D,L,0} \quad (9)$$

and the concentrations $C_{A,L,0}$, $C_{B,L,0}$, $C_{C,L,0}$ and $C_{D,L,0}$ satisfy $R_A=0$ in eq. (4). The boundary condition for $x=\infty$ can also be derived with the assumption of chemical equilibrium for the bulk of the liquid for a given solute loading:

$$t > 0 \text{ and } x = \infty: C_{A,L} = C_{A,L,0}, C_{B,L} = C_{B,L,0}, C_{C,L} = C_{C,L,0} \text{ and } C_{D,L} = C_{D,L,0} \quad (10)$$

However, in case of irreversible chemical reactions ($K=\infty$) eq.(10) can only be used for situations where $C_{A,L,0}=0$ (or $C_{B,L,0}=0$ which is identical to physical absorption), because for concentrations of A different from zero the liquid bulk is not at equilibrium and therefore a reaction will occur. In the latter case boundary condition (10) is not valid and a material balance over the liquid bulk must be used instead. Note that the application of eqs. (9)-(10) is only valid if the equilibrium composition is used. The second boundary condition is obtained by assuming that the species B, C, and D are non-volatile and that $C_{A,L}=C_{A,L,i}$:

$$t \geq 0 \text{ and } x=0: C_{A,L} = C_{A,L,i}, \frac{\partial C_{B,L}}{\partial x} = \frac{\partial C_{C,L}}{\partial x} = \frac{\partial C_{D,L}}{\partial x} = 0 \quad (11)$$

In case the reaction rate can be regarded as instantaneous compared to the mass transfer rate, the boundary condition (11) is no longer valid and the gradients of B, C and D are not necessarily zero to assure non-volatility (Versteeg et al., 1989). Unfortunately, generally valid solutions for these four non-linear partial differential equations (5)-(8) cannot be obtained analytically and therefore numerical solution techniques are required. However, only for a few very special cases analytical solutions could be obtained. An alternative approach in finding a method for the calculation of the mass transfer rate, i.e. the enhancement factor, is by approximation and/or linearization. It is clear that for other mass transfer models, i.e., film or surface renewal model, (differential) equations equivalent to eqs. (5)-(8) can be derived.

2.2. Irreversible Chemical Reaction.

In this section absorption processes accompanied by a single irreversible reaction with (m,n)th-order kinetics will be treated.

2.2.1. Analytical Solutions.

In 1932, Hatta (1932) presented for the film model an analytical solution for the description of mass transfer followed by a first order irreversible reaction:



For this absorption process the following mass balance has to be solved:

$$D_A \frac{d^2 C_{A,L}}{dx^2} = k_1 C_{A,L} \quad 0 \leq x \leq \delta \quad (13)$$

As the reaction is irreversible the conversion of A which will be transported to the liquid bulk must also be taken into account, in the present derivation it is assumed that no reactant enters the bulk apart from the gas phase and that the amount of reactant in the outlet stream is very negligible compared to the conversion rate. This amount can be

implemented in one of the two boundary conditions required to solve eq. (13):

$$x=0, C_{A,L}=C_{A,Li} \quad (14a) \quad \text{and} \quad x=\delta, D_A \left(\frac{dC_{A,L}}{dx} \right)_{x=\delta} = k_1 C_{A,L} V_{L,bulk} \quad (14b)$$

Resulting in:

$$J_A = \frac{D_A}{\delta} C_{A,Li} \phi_A \frac{\phi_A (AL-1) + \tanh \phi_A}{\phi_A (AL-1) \tanh \phi_A + 1} \quad (15)$$

In eq. (15) AL is the 'Hinterland ratio' defined as the ratio between the total reaction phase volume and the volume of the (stagnant) mass transfer film of the reaction phase and ϕ_A is the wellknown Hatta-number:

$$AL = \frac{1-\varepsilon}{\delta_a} = \frac{(1-\varepsilon)k_L}{a.D_A} \quad (16) \quad \phi_A = \delta \sqrt{\frac{k_1}{D_A}} = \frac{\sqrt{k_1 D_A}}{k_L} \quad (17)$$

For practical conditions in gas-liquid contactors usually $AL \gg 1$ and $(AL-1)\phi_A^2 \gg 1$, therefore eq.(15) can be reduced to:

$$J_A = \frac{D_A}{\delta} C_{A,Li} \frac{\phi_A}{\tanh \phi_A} = k_L C_{A,Li} E_A \quad (18) \quad E_{A,film} = \frac{\phi_A}{\tanh \phi_A} \quad (19)$$

From eq.(18) it can be concluded that the enhancement factor for mass transfer followed by a first order irreversible reaction for the film model is a function of the Hatta-number. Also for both the penetration and the surface renewal model analytical expressions for E_A for first order irreversible reaction can be derived (Danckwerts, 1970):

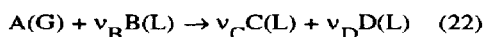
$$E_{A,surf.ren.} = \sqrt{1 + \phi_A^2} \quad (20) \quad E_{A,pen.} = \phi_A \left[\left\{ 1 + \frac{\pi}{8\phi_A^2} \right\} \operatorname{erf} \left[\sqrt{\frac{4\phi_A^2}{\pi}} \right] + \frac{1}{2\phi_A} \exp\left(-\frac{4\phi_A^2}{\pi}\right) \right] \quad (21)$$

The difference between the enhancement factors for these three absorption models is very small. The largest deviations are obtained for $\phi_A=1$: only 7.6%!

For all other processes in which mass transfer is followed by chemical reactions it is not possible to present analytically derived relations for the calculation of the enhancement factor that are valid over wide range of process conditions. As already mentioned above besides numerically derived solutions, an alternative approach is the calculation of the mass transfer rate, i.e. the enhancement factor, by means of an approximation and/or linearization of the actual absorption process.

2.2.2. Approximation techniques for irreversible reactions.

Van Krevelen and Hoftijzer (1948) were the first who presented an approximation method for the description of the absorption of A into a reactive liquid:



with:

$$R_A = -k_2 C_{A,L} C_{B,L} \text{ mol.m}^{-3} \cdot \text{s}^{-1} \quad (23)$$

For the solution of this absorption process eqs.(5) and (6) have to be solved simultaneously. It should be noted that for the film model the time derivatives in (5) and (6) are equal to zero. In order to obtain an analytical solution van Krevelen and Hoftijzer approximated the actual concentration profiles of both reactants according to Fig. 1. From Fig. 1 it is clear that the essential part of the approximation is the definition of a very small zone near the interface in which a (pseudo-) first order reaction occurs, i.e. no concentration gradient for reactant B. By means of the van Krevelen-Hoftijzer approximation an implicit expression for the enhancement factor can be derived:

$$E_A = \frac{\phi_A \sqrt{\frac{E_{A\infty} - E_A}{E_{A\infty} - 1}}}{\tanh \phi_A \sqrt{\frac{E_{A\infty} - E_A}{E_{A\infty} - 1}}} \quad (24)$$

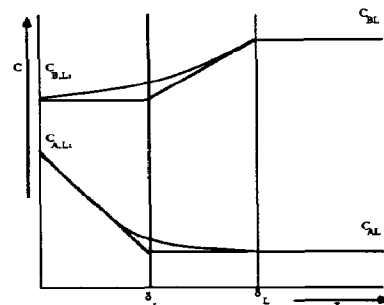


Figure 1: Concentration profile approximation according to van Krevelen and Hoftijzer.

$$E_{A\infty,film} = 1 + \frac{D_B C_{B,L}}{\nu_B D_A C_{A,Li}} \quad (25)$$

From eq.(24) it can be concluded that besides the Hatta-number, ϕ_A , an additional dimensionless group is introduced; the maximum attainable enhancement factor, $E_{A\infty}$. The accuracy of this expression obtained by means of approximation is remarkably good, compared with numerical solutions whose deviation is always less than 3% (de Santiago and Farina, 1970). Marek and Schöngut (1979) fitted several algebraic relations to their numerical solution of the film model, however, the major part of these approximated relations lack any physical meaning.

From eq. (25) it can be concluded that some resistance against mass transfer in the gas phase will affect the value of the enhancement factor because owing to this resistance $C_{A,Li}$ will be reduced. For this situation Karlsson and Bjerle (1980) and Patwardhan (1981) presented relations which were modified for the effect of the gas phase resistance. In 1961 Brian et al. (1961) showed that eq. (24) also can be used for the penetration model if the expression for the instantaneous enhancement factor is replaced, eq. (25), for the penetration analogy:

$$E_{A\infty,pen} = \sqrt{\frac{D_A}{D_B}} + \sqrt{\frac{D_B}{D_A}} \frac{C_{B,L}}{v_B C_{A,Li}} \quad (26) \quad E_A = \frac{E_{A,ps}^2}{2(E_{A\infty}-1)} \left\{ \left[1 + 4 \frac{E_{A\infty}(E_{A\infty}-1)}{E_{A,ps}^2} \right]^{0.5} - 1 \right\} \quad (27)$$

By means of additional approximations Yeramian et al. (1970) modified eq.(24) to an explicit relation for the penetration model, eq. (27) with $E_{A,ps}$ the enhancement factor obtained for pseudo first order reaction according to eq. (21). Wellek et al. (1978) reevaluated the above mentioned approximate solutions and derived a new expression which could be used for the estimation of the enhancement factors for second order irreversible reactions:

$$\frac{1}{(E_A-1)^n} = \frac{1}{(E_{A\infty}-1)^n} + \left(\frac{\phi_A}{\tanh \phi_A} - 1 \right)^{-n} \quad (28)$$

The best results were obtained for $n=1.35$.

Hikita and Asai (1963, 1964) extended the van Krevelen-Hoftijzer approach for irreversible reactions of higher orders:

$$R_A = k_{m,n} C_{A,L}^m C_{B,L}^n \quad \text{mol.m}^{-3} \cdot \text{s}^{-1} \quad (29) \quad \tilde{R}_A = \frac{2}{m+1} k_{m,n} C_{A,Li}^{m-1} C_{A,L} C_{B,L}^n \quad (30)$$

Compared to van Krevelen and Hoftijzer they assumed that the concentration of the liquid phase reactant B was constant over the mass transfer film and equal to the interface concentration. However, for these higher reaction orders the approximation of the concentration profiles only is not sufficient because of the non-linearity of the reaction rate expression. Therefore Hikita and Asai also linearized eq. (29), resulting in eq.(30). From the work of Hikita and Asai it was concluded that the relation derived by van Krevelen and Hoftijzer for the calculation of the enhancement factor eq.(24) was also satisfactory accurate for higher order reactions if the Hatta-number was calculated according to:

$$\phi_A = \frac{\sqrt{\frac{2}{m+1} k_{m,n} C_{A,Li}^{m-1} C_{B,L}^n D_A}}{k_L} \quad (31)$$

If $E_{A\infty}$ is calculated with eq. (25) the film model and with eq. (26) the penetration model enhancement factor is obtained respectively. For the surface renewal model Yeramian et al. (1970) and DeCoursey (1974) presented in an explicit expression for the calculation of the enhancement factor for a second order irreversible reaction:

$$E_A = \frac{\phi_A^2}{2(E_{A\infty}-1)} \left\{ \left[1 + \frac{4[(E_{A\infty}-1)^2 + E_{A\infty}\phi_A^2(E_{A\infty}-1)]}{\phi_A^4} \right]^{0.5} - 1 \right\} \quad \text{Yeremian et al.} \quad (32)$$

$$E_A = -\frac{\phi_A^2}{2(E_{A\infty}-1)} + \sqrt{\left[\frac{\phi_A^4}{4(E_{A\infty}-1)^2} + \frac{E_{A\infty}\phi_A^2}{(E_{A\infty}-1)} + 1 \right]} \quad \text{DeCoursey} \quad (33)$$

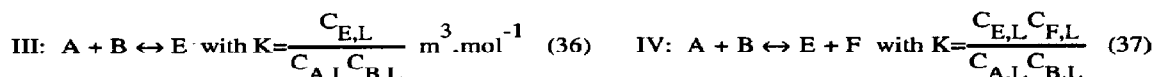
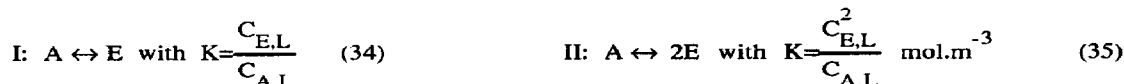
2.3. Reversible Chemical Reaction

In this section absorption processes accompanied by a single reversible reaction according to eq. (3) will be treated for reaction rate expressions similar to eq. (4).

2.3.1. Analytical Solutions.

There are no general applicable analytically derived relations available for the calculation of the enhancement factor for this type of absorption processes. However, Olander (1960) derived for some asymptotic cases, processes in which the reaction rates are instantaneous compared to the mass transfer rates, analytical expressions for the enhancement factor.

For the film model Olander studied the following four reactions:



It should be noted that for the conditions studied by Olander, at all places in the stagnant film the reactants and products

are at equilibrium, i.e., $R_A=0$. For the above mentioned cases the enhancement factors can be calculated with:

$$\text{reaction I: } E_{A\infty} = 1 + \frac{D_E}{D_A} K \quad (38)$$

$$\text{reaction II: } E_{A\infty} = 1 + \frac{D_E}{D_A} \frac{\sqrt{0.25K}}{\sqrt{C_{A,Li}} + \sqrt{C_{A,L0}}} \quad (39)$$

$$\text{reaction III: } E_{A\infty} = 1 + \frac{D_B}{D_A} \frac{C_{B,L0}}{C_{A,Li} + \frac{D_B}{D_E} K} \quad (40)$$

$$\text{reaction IV: } E_{A\infty} = 1 + \frac{D_B}{D_A} \frac{\psi}{C_{A,Li} - C_{A,L0}} \quad (41)$$

with:

$$\begin{aligned} \psi = \frac{1}{2} \left\{ \left[\left(\frac{D_F}{D_E} - 1 \right) \sqrt{K C_{A,L0} C_{B,L0}} + \frac{D_F}{D_B} C_{A,Li} K \right]^2 + 4 \left[\frac{D_B}{D_E} C_{B,L} + \sqrt{K C_{A,L0}} \right] \left(\frac{D_F}{D_B} K C_{A,Li} \right) \right\}^{0.5} \\ - 0.5 \left[\left(\frac{D_F}{D_E} + 1 \right) \sqrt{K C_{A,L0} C_{B,L0}} + \frac{D_F}{D_B} K C_{A,Li} \right] \quad (41a) \end{aligned}$$

Besides the above mentioned cases for the film model, Olander presented for reactions I, II and III also solutions for the surface renewal theory:

$$\text{reaction I: } E_{A,\text{surf.ren.}} = \sqrt{\left(1 + \frac{D_E}{D_A} K \right) (1 + K)} \quad (42)$$

$$\text{reaction II: } E_{A,\text{surf.ren.}} = \frac{\sqrt{C_{A,Li}} + \frac{\sqrt{K}}{4} \frac{D_E}{D_A}}{\left(\frac{C_{A,Li}}{b} \right)^{0.5} \exp\left(\frac{a^2}{b}\right) \text{erfc}\left(\frac{a}{\sqrt{b}}\right)} \quad (43)$$

with:

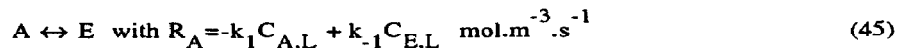
$$a = \frac{\frac{\sqrt{K} D_E}{4} (C_{A,Li} - C_{A,L0})}{C_{A,Li} \left(2\sqrt{C_{A,Li}} + \frac{\sqrt{K} D_E}{2 D_A} \right) \exp\left(\frac{a^2}{b}\right) \left(\frac{\pi}{b} \right)^{0.5} \text{erfc}\left(\frac{a}{\sqrt{b}}\right)} \quad (43a)$$

$$b = 0.5 \left[\frac{\sqrt{C_{A,Li}} + \frac{\sqrt{K}}{4}}{\sqrt{C_{A,Li}} + \frac{\sqrt{K} D_E}{4 D_A}} \right] + a^2 \left(\frac{12\sqrt{C_{A,Li}} D_A}{\sqrt{K} D_E} + 1 \right) \quad (43b)$$

It is clear that for reaction II an implicit relation for the estimation of the enhancement factors is obtained and that its use is a cumbersome routine. For reaction III only an expression could be derived in case it was assumed that the diffusivities of reactants A and B and product E were equal:

$$\text{reaction III: } E_{A\infty,\text{surface renewal}} = 1 + \frac{C_{B,Lc}}{C_{A,Li} + \frac{1}{K}} \quad (44)$$

Huang and Kuo (1965) presented for the first-order reversible reaction:



analytically derived solutions for the film model, surface renewal and the film-penetration theory.

For the surface renewal theory:

$$E_{A,\text{surface renewal}} = \frac{\mu_1 \mu_2 (\mu_1 + \mu_2) \sqrt{\phi_A}}{\mu_1^2 + \mu_1 \mu_2 + \mu_2^2 - \left(1 + \frac{1}{\phi_A} \right)} \quad (46)$$

with:

$$\mu_1 = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{D_E K}{D_A} + \left(1 + \frac{D_E}{D_A} \right) \frac{1}{\phi_A} + \sqrt{\left[1 - \frac{D_E K}{D_A} + \left(1 - \frac{D_E}{D_A} \right) \frac{1}{\phi_A} \right]^2 + \frac{D_E}{D_A} 4K} \right\}^{0.5} \quad (46a)$$

$$\mu_2 = \frac{1}{\sqrt{2}} \left\{ 1 + \frac{D_E K}{D_A} + \left(1 + \frac{D_E}{D_A} \right) \frac{1}{\phi_A} - \sqrt{\left[1 - \frac{D_E K}{D_A} + \left(1 - \frac{D_E}{D_A} \right) \frac{1}{\phi_A} \right]^2 + \frac{D_E}{D_A} 4K} \right\}^{0.5} \quad (46b)$$

For the the film model they obtained:

$$E_{A,\text{film}} = \left[1 + \frac{D_E}{D_A} K \right] \left[\frac{D_E}{D_A} K + \frac{\tanh\left(\left[1 + \frac{D_E}{D_A} K\right]^{0.5} \sqrt{\phi_A}\right)}{\left[1 + \frac{D_E}{D_A} K\right]^{0.5} \sqrt{\phi_A}} \right]^{-1} \quad (47)$$

and for the relation of the film-penetration theory the reader is referred to the paper of Huang and Kuo (1965).

The applicability of the analytically derived relations for the calculation of the enhancement factors for gas absorption accompanied by a single reversible reaction is limited use as they are only valid for asymptotic cases. However, these relations are very useful for the validation of numerically solved models or to check approximations.

2.3.2. Approximation techniques for reversible reactions.

Onda et al. (1970a and 1972) presented approximate solutions for both film and penetration model. They used the same approximation technique as Hikita & Asai (1963), however, as Onda et al. studied a reversible reaction they had to extend the linearization of to the reverse rate equation in order to arrive at a set of equations which could be solved analytically:

$$\tilde{R}_A = -\frac{2}{m+1} k_{m,n} C_{A,L}^{m-1} C_{B,L}^n C_{A,L} - \frac{2}{p+1} k_{t,v} C_{C,L}^{t-1} C_{D,L}^v C_{C,L} \quad \text{mol.m}^{-3} \cdot \text{s}^{-1} \quad (48)$$

Furthermore, they assumed that the concentrations of reactant B and product D are constant over stagnant film and equal to the interface concentrations:

$$C_{B,L} = C_{B,Li} \quad \text{for } 0 \leq x \leq \delta \quad (49) \quad C_{D,L} = C_{D,Li} \quad \text{for } 0 \leq x \leq \delta \quad (50)$$

Because Onda et al. treated the reaction products E and F in a different way in the linearization of the reaction rate equation a somewhat strange expression for the equilibrium constant is obtained:

$$K = \frac{m+1}{t+1} \frac{C_{C,L}^t C_{D,L}^v}{C_{A,L}^m C_{B,L}^n} \quad (51)$$

which is a function of the reaction orders m and t . Furthermore, the reaction rate expression, R_A , should be zero at $x=\delta$ indicating that in the liquid bulk the equilibrium composition is maintained. For the linearized rate expression used by Onda, R_A can have values different from zero at $x=\delta$ and only for the very special case that $C_{A,L0}=C_{C,L0}=0$ this condition is always fulfilled.

The approximate solutions of Onda were checked with numerical solutions by De Lind van Wijngaarden et al. (1986) and Versteeg et al. (1989). The maximum deviation from the numerical model is always less than 2% for the film model. However, for reactions with $m \neq t$ the Onda approximation is not able to obtain realistic values for the enhancement factor (i.e. ≥ 1) in case the reverse reaction cannot be neglected. Therefore the Onda approximation for the film model can only be applied satisfactory if the values for m and t are equal. In case only one product is formed this approximation can be applied without the restriction that $m=t$. For the penetration theory approximation the same conclusions are valid and the maximum deviation was always less than 7%. It should be noted that this approximation can only be used in case all the diffusivities are the same which restricts its applicability. Overall it can be concluded that the linearization of the reaction term according to Hikita & Asai (1963) cannot be applied generally to reversible reactions if the reaction products are treated differently in the linearization of the rate expression.

For the surface renewal theory DeCoursey (1982) derived an approximate analytical solution for the reversible reaction according to eq.(3). He obtained this solution by changing the instantaneous concentrations to time mean concentrations by taking "s-multiplied" Laplace transforms, similar to the Danckwerts' surface renewal model. In order to obtain an integrable set linear differential equations with constant coefficients he made the following assumptions:

- the diffusivities of all species are equal.
- the equilibrium at any point can be expressed by $C_{A,Le} = (C_{C,L} C_{D,L}) / (K C_{B,L})$
- $C_{B,L}$ is equal to $C_{B,Li}$ near the interface according to van Krevelen & Hoftijzer (1948).
- the reaction rate can be described with $R_A = -K_1(C_{A,L} - C_{A,L0}) + f_1(x)$.
- at $x=\infty$ R_A can be expressed by $R_A = -k_2 C_{B,Li}(C_{A,L} - C_{A,L0}) = 0$ and at $x=0$ by $R_A = -k_2 C_{B,Li}(C_{A,L} - C_{A,Le})$

The approximate solutions of DeCoursey were also checked verified by De Lind van Wijngaarden et al. (1986) and Versteeg et al. (1989). The deviation with the numerical solutions for other reactions was always less than 10%. The DeCoursey approximation results in accurate enhancement factors for the surface renewal model over a wide range of process conditions. The condition that the diffusivities of all species considered must be equal is a substantial restriction for the applicability. Therefore DeCoursey and Thring (1989) modified this method to systems with unequal diffusivities of the reactants and products. This modified DeCoursey approach was numerically evaluated by Winkelman et al. (1992) and they concluded that the approximate solution had a mean deviation of 3.1% and a maximum of 14%.

2.3.3. Numerical solutions for reversible reactions.

With the tremendous speed of innovation of the computational power of the computers the use of numerical techniques for the description of mass transfer accompanied by (reversible) reaction(s) became more frequent. Numerically solved absorption models for mass transfer followed by a single reversible reaction according to eq.(3) were presented by Perry & Pigford (1953), Secor & Beutler (1967), Porter et al. (1971) and Versteeg et al. (1989). They all applied the finite-difference solution method on the set of differential equations of the penetration theory. The work of Perry & Pigford (1953) can be regarded as a first introduction in calculating mass transfer rates numerically. The publications of Secor & Beutler (1967) and Porter et al. (1971) are of restricted use because a limited range of conditions has been studied and the influence of solute loading and the behaviour under desorption conditions has been omitted, or the applicability has been restricted for a few stoichiometric schemes respectively. Moreover, the solutions of Secor & Beutler, specifically in case the chemical equilibrium constant was equal to one, must be used with caution because of inaccuracies in the results (DeCoursey, 1982 and Winkelman et al., 1992).

The main goal of the application of a numerical approach is to produce the concentration profiles for the film model as solution of a system of coupled non-linear ordinary differential equations with two point boundary conditions. After solving this set of equations the enhancement factor can be calculated easily derived from the concentration profiles. In the penetration (Higbie) model the concentration profiles are time-dependent: they develop as solution of a system of coupled non-linear parabolic partial differential equations subject to specified initial and two point boundary conditions.

Cornelisse et al. (1980), demonstrated that the application of this scheme to processes with mass transfer accompanied by complex reversible reactions resulted in a very powerful and reliable numerical methodology. In order to reduce the required computational time and to improve on the accuracy Versteeg et al. (1989) added some additional numerical features of which the transformation of the spatial coordinate turned out to be very effective:

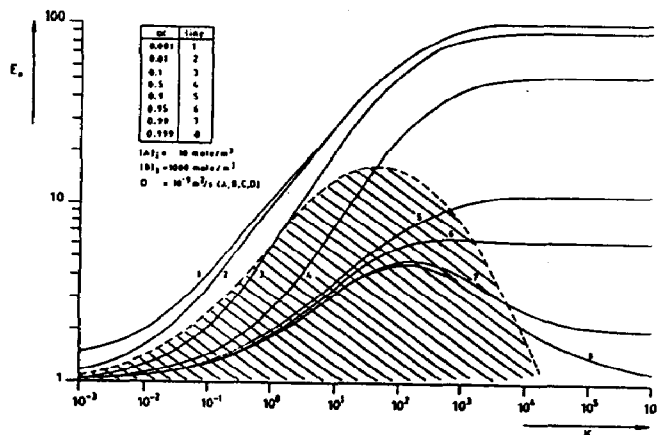


Figure 2: Enhancement factor as function of the equilibrium constant, K , for various solute loadings. The dashed line represents the conditions where no net mass transfer occurs, under this line desorption prevails. Film model.

$$\tau = \operatorname{erf}\left(\frac{x}{\sqrt{4D_1t}}\right) \quad (52)$$

It should be noted that Porter et al. (1971) also applied the transformation according to eq.(52).

An additional advantage of the implementation of eq.(52) occurs in the beginning, when the most rapid changes occur, due to the sudden onset of the interface condition eq.(11). Especially the Newton-Raphson linearization of the non-linear reaction term, eq. (4), using estimates of a previous time level (Cornelisse et al. (1980)) may be awkward just because of the large changes from one time level to another. In this new coordinate system, however, the onset of the interface conditions is not abrupt but gradual, starting from zero and in the interior all the differences will be gradually rising. Accordingly, the estimates in the linearization of the reaction term will be much more accurate. As a consequence of the implementation of additional numerical features the computational time required per simulation could be reduced from several minutes on a Digital DEC2060 to about 1 minute on a personal computer with mathematical coprocessor (Tulip 386AT/25) (Bosch et al., 1989a).

As was already mentioned in section 2.2.2 the occurrence of resistance against mass transfer in the gas phase can have an significant effect on the enhancement factor. Therefore Cornelisse et al. (1980) and Versteeg et al. (1989) used in their numerical absorption models for the calculation of the enhancement factor a modified boundary condition for eq.(11):

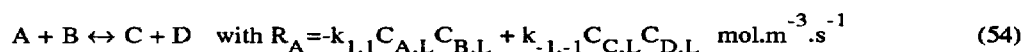
$$k_G(C_{A,G} - C_{A,Gi}) = -D_A \left(\frac{\partial C_{A,L}}{\partial x} \right)_{x=0} \quad (11a) \quad \left(\frac{\partial C_{B,L}}{\partial x} \right)_{x=0} = \left(\frac{\partial C_{C,L}}{\partial x} \right)_{x=0} = \left(\frac{\partial C_{D,L}}{\partial x} \right)_{x=0} = 0 \quad (11b)$$

The use of eq.(11a) instead of $C_{A,L} = C_{A,Li}$ at $x=0$ is convenient in view of the applicability of the model for absorber calculations especially for those cases where a part of the resistance against mass transfer is situated in the gas phase.

In Fig. 2 and 3 the effect of the reversibility of the reaction on the enhancement factor is demonstrated for $k_G \rightarrow \infty$. In Fig. 2 the enhancement factor according to the film model is presented as a function of the chemical equilibrium constant for several solute loadings, α :

$$\alpha = C_{A,L,\text{total}} / C_{B,L,\text{total}} \quad (53)$$

for the reaction:



and the reaction rate is instantaneous compared to the mass transfer rate. For high values of $K(=k_{1,1}/k_{-1,-1})$ this situation is identical to absorption followed by an instantaneous irreversible reaction with respect to mass transfer and the enhancement factor, E_A , can be calculated with eq. (25).

The enhancement factor increases with the equilibrium constant because the reverse reaction rate constant decreases and therefore the effect of the reverse reaction. However, for extremely high solute loadings the bulk concentration of B further decreases with increasing equilibrium constant and, although the effect of the reverse reaction can be neglected, the enhancement factor shows a maximum and decreases until the equilibrium composition of the liquid remains constant and then the enhancement factor can be calculated with eq. (25). In Fig. 2 two regimes are shown, the dashed area represents the conditions where desorption prevails and the area above the absorption regime. At the boundary of the two areas no net mass transfer occurs. In Fig. 3 the enhancement factor according to the penetration model is presented as a function of the Hatta-number for several equilibrium constants and a relatively low solute loading, $\alpha=10^{-3}$, for the same reaction as mentioned above.

In Fig. 3 can be seen that the reversibility also has a pronounced effect on the enhancement factor for reactions with finite reaction rate constants. It should be noted that the deviation from the line $E_A=\phi_A$, indicating that diffusion limitation of component B occurs, is starting at lower Hatta-numbers with decreasing equilibrium constant.

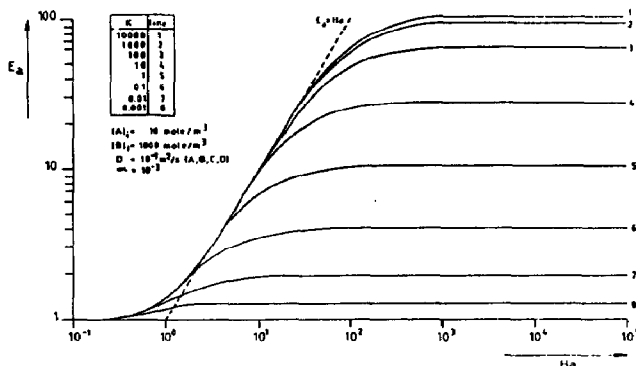


Figure 3: Enhancement factor as function of the Hatta-number for various equilibrium constants. Penetration model.

2.4. Simultaneous absorption of two gases.

This group of processes can be divided into two groups; simultaneous absorption of two gases reacting with each other in the liquid phase and simultaneous absorption of two gases into a liquid which contains one (or more) reactants. Ramachandran and Sharma (1971) presented an extensive review on these processes.

2.4.1. Simultaneous absorption and reaction of two gases.

Typical examples of this type of processes are the absorption of NH_3 and CO_2 in water and ethylene and hydrogen chloride into an ethylchloride solution. Roper et al. (1962) studied the simultaneous absorption and reaction of two gases in a liquid and described this process with the penetration theory. The mass balances were numerically solved for a bi-molecular irreversible reaction between both gases. For irreversible reactions of $(m,n)^{\text{th}}$ -order Hikita et al. (1977) presented for both film model and penetration theory approximate solutions for the calculation of the enhancement factor. Their approximate relations were checked with numerical solutions and the agreement was good. For both studies must be noted that the results depend on the boundary conditions used during the solution of the mass balance. Zarzycki et al. (1981) presented additional approximate solutions for irreversible reactions and compared the solutions with those of Hikita et al. (1977).

Reversible reactions have not been studied so far.

2.4.2. Simultaneous absorption of two gases into a reactive liquid.

The removal of CO_2 and H_2S from acidic gases by means of reversible absorption into an aqueous alkanolamine solution is a very important process. Therefore it is not surprising that a large amount of research has been invested on the description of this simultaneous absorption process. Because both gases react reversibly with the amine and as an interaction between the reaction products occurs, it is clear that only by means of numerical techniques a correct description of this absorption process can be obtained. Cornelisse et al. (1980) presented a numerically solved absorption model for the simultaneous absorption of CO_2 and H_2S into an aqueous diisopropanolamine solvent.

For the film model Onda et al. (1970b) presented an approximate solution for the absorption of two gases into a reactive liquid in which two irreversible reactions of $(m,n)^{\text{th}}$ -order take place. They used the Hikita and Asai (1963) approach for the description of this absorption process. The first numerically solved absorption model was presented by Goetler and Pigford (1971). However, they restricted themselves to processes with irreversible chemical reactions and therefore for e.g., acid-gas treating processes this work is of limited use. Further approximate solutions were presented by Cornelisse et al. (1977) and Hikita et al. (1979) for the film model and irreversible reactions, with one gas reacting instantaneously. No significant difference exists between these two models. Barreto and Farina (1982) derived/fitted algebraic relations for the calculation of the enhancement factors for the above mentioned asymptotic situations.

As mentioned above Cornelisse et al. (1980) were the first who presented an absorption model, based on the penetration theory, in which the reversibility of the reactions were taken into account. As a result of this a numerical solution technique had to be applied. From the work of Cornelisse et al. it must be concluded that for absorption processes with (complex) reversible reactions only by means of numerically solved absorption models reliable information on the process can be obtained. An outstanding example of this conclusion is the phenomenon forced desorption which Cornelisse et al. observed as a result of numerical process simulations. Forced desorption occurs due to the simultaneous absorption of another reactive species and the reversible interactions that occur between the various reactants and products

near the gas-liquid interface. Its characteristics are that the sign of the concentration difference is no exclusive indication of the direction of the mass transfer process. In Fig. 4 calculated concentration profiles at conditions of forced desorption are presented for the simultaneous absorption of CO_2 and H_2S into an aqueous amine solution. Blauwhoff and van Swaaij (1985) verified experimentally the phenomenon forced desorption. Bosch et al. (1989) modified the Cornelisse absorption model in order to make it more general applicable, Edgerton et al. (1986) developed a similar model.

2.5. Absorption of a single gas and parallel reversible reactions with liquid phase reactants.

In the process industry, operations accompanied by several parallel reversible chemical reactions occur very often. A frequently encountered process in which two parallel reactions take place is the absorption of CO_2 (or H_2S) in an aqueous alkanolamine solution. In this solution the CO_2 (or H_2S) reacts with the alkanolamine and the hydroxyl ions which are present in the liquid due to the protonation of the amine. Even in the case of single gas absorption in amine gas-treating processes several parallel chemical reactions may occur because the purity of the amine used is less than 100% and usually the contaminants are other very reactive amines.

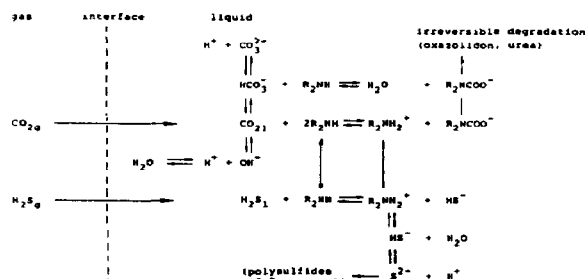


Figure 4a: Reaction scheme for the simultaneous absorption of H_2S and CO_2 in an aqueous alkanolamine solution.

2.5.1. Parallel reactions without interaction.

For irreversible reactions it can easily be derived that the enhancement factor for the process with parallel reactions is smaller or equal to the summation of the enhancement factors for the single reactions. In case all reactions can be regarded as instantaneous with respect to mass transfer the enhancement factor for the system with the multiple reactions can be calculated with:

$$E_{A\infty, \text{multiple}} = \left(\sum_{j=1}^n E_{A, \text{single}} - 1 \right) + 1 \quad (55)$$

$$E_{A, \text{multiple}} = \sqrt{\sum_{j=1}^n (E_{A, \text{single}})^2} \quad (56)$$

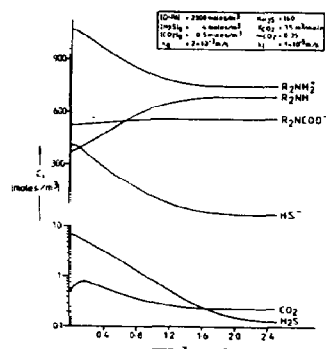


Figure 4b: Calculated concentration profiles at the end of the contact time under forced desorption conditions. CO_2 diffuses partly towards the gas phase, although based on the overall concentration difference absorption would have been expected.

the maximum attainable enhancement factor can be calculated for the film model according to eq.(25).

For the asymptotic situation of pseudo first-order irreversible reaction kinetics for the single reactions the enhancement factor for the multiple reaction process can be derived according to eq. (56). Because in the pseudo first-order regime the enhancement factor for the single process is equal to the Hatta-number. The third asymptotic situation occurs in case of slow reaction rates for which also a simple relation for the calculation of the enhancement factor can be derived. Therefore no enhancement of the absorption process occurs and the enhancement factor is equal to unity for both the single and multiple reactions. Chang and Rochelle (1982) concluded that for a system of noninteracting multiple reactions, each constituting single reaction contributes one additive term to the overall enhancement factor.

The three above mentioned asymptotic situations for irreversible reactions were extended by Jhaveri (1969) who presented approximate solution methods for two parallel second order reactions and one instantaneous reaction and the other pseudo first order. For the latter situation Alper (1972) questioned whether the Jhaveri method would lead to realistic values of the enhancement factor. Alper (1973) presented the penetration analogy of eq.(55) for the penetration theory:

$$E_{A\infty, \text{multiple}} = \left[\text{erf} \left(\frac{\beta}{\sqrt{D_A}} \right) \right]^{-1} \quad (57)$$

and β must be derived from:

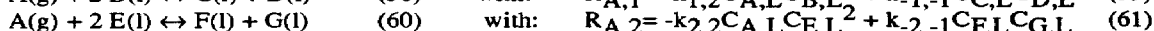
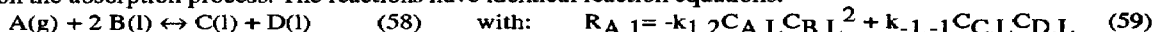
$$\frac{C_{A, L} \exp \left(-\frac{\beta^2}{D_A} \right)}{\text{erf} \left(\frac{\beta}{\sqrt{D_A}} \right)} = \sum_{j=1}^n \frac{1}{v_{B, j}} \sqrt{\frac{D_{B, j}}{D_A}} \frac{C_{B, j, L} \exp \left(-\frac{\beta^2}{D_{B, j}} \right)}{\text{erf} \left(\frac{\beta}{\sqrt{D_{B, j}}} \right)} \quad (57a)$$

Onda et al. (1970b) presented for the film model an approximate solution for two parallel irreversible reactions of $(m, n)^{\text{th}}$ -order kinetics. They approximated the absorption process along the lines as discussed in section 2.3.2 (Onda et al. (1970a)), however, an two additional assumptions were required in order to be able to solve the resulting equations. Onda et al. used quadratic relations for the concentration profile of reactant B and the ratio of C/B .

2.5.2. Parallel reactions with interaction.

In case the reactions are reversible it is not possible to predict the overall enhancement factor of the absorption process by means of equations similar to (55), (56 and (57). Therefore the effect of reversibility must be studied with numerically solved models. Chang and Rochelle (1982) presented for some special cases relations for the enhancement factor for multiple reversible reactions derived for close-form solutions of the film theory. Li et al (1974) studied absorption processes for some typical reactions like first- and second-order parallel reaction and one reaction proceeding via two routes to different products. Versteeg et al. (1990) developed a numerical absorption model for absorption processes accompanied with multiple reversible reactions. Optional in this model were interactions between the liquid phase reactants and products.

For a system consisting of two parallel reactions with a moderate and a low value of the equilibrium constant respectively it will be demonstrated that only numerically solved absorption models can be used for obtaining accurate information on the absorption process. The reactions have identical reaction equations:



For information on the values of the physico-chemical constants is referred to Table 1.

In Table 2 the outcome of the calculations for the enhancement factor is presented together with the enhancement factor which would be attained if the simulations were performed for the individual systems.

Table 2. Results simulation for the system A+2B and A+2E without interaction.

	case 1	case 2	case 3	case 4
$E_{\text{reaction (57)}}$	507	221	507	276
$E_{\text{reaction (58)}}$	198	198	194	198
E_{parallel}	2530	792	2257	1499

Table 1: Conditions for the simulation for the system A+2B and A+2E without interaction.

[A] _g	0.1 mol.m ⁻³
[B] _l	100 mol.m ⁻³
[E] _l	2000 mol.m ⁻³
k_1	0.60 mol.mol ⁻¹ .s ⁻¹
k_g	1*10 ⁻⁵ m.s ⁻¹
$k_{1,2}$ (B)	1*10 ⁶ m ⁶ .mol ⁻² .s ⁻¹
$k_{-1,-1}$ (B)	1*10 ⁵ m ³ .mol ⁻¹ .s ⁻¹
$k_{1,2}$ (A)	1*10 ⁻³ m ⁶ .mol ⁻² .s ⁻¹
$k_{-1,-1}$ (A)	1*10 ⁻⁵ m ³ .mol ⁻¹ .s ⁻¹
case 1	$D_i = 1*10^{-9}$ m ² .s ⁻¹
case 2	$D_B = 1*10^{-10}$ m ² .s ⁻¹
case 3	$D_E = 1*10^{-10}$ m ² .s ⁻¹
case 4	$D_C=D_D = 1*10^{-10}$ m ² .s ⁻¹

The first reaction (58) is instantaneous with respect to mass transfer and the second reaction (59) can be regarded as a pseudo first-order reaction. Contrary to the situation for irreversible reactions the enhancement factor for reversible multiple reactions can be substantially higher as can be seen in Table 2. This striking effect can be explained if the concentration profiles of the reactants and products of the multiple system is compared with those of the single systems, see Fig. 5. It should be noted that both concentration and spatial coordinate are dimensionless. The liquid-phase components are normalized on the bulk concentrations of each reactant respectively, and the gas-phase component on the bulk gas-phase concentration corrected for the solubility. From Fig. 5 it can be concluded that owing to the presence of E the concentration of B near the gas-liquid interface was increased by means of the interaction of the reactions (58) and (59) according to:



the interaction of these reactions leads to:

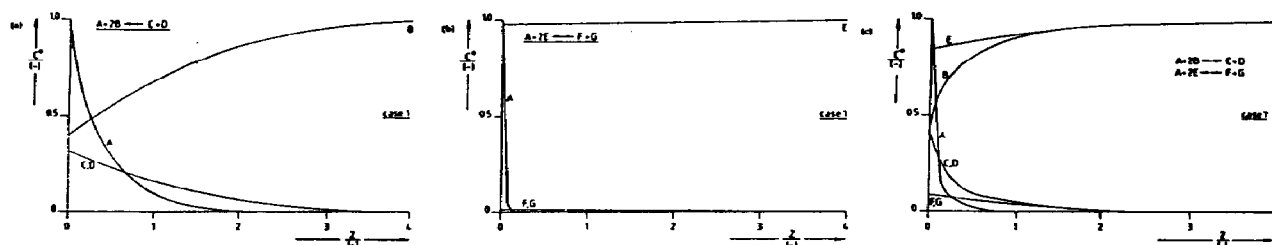


Figure 5: Dimensionless concentration profiles for (a) the system $A + 2B \leftrightarrow C + D$, the system $A + 2E \leftrightarrow F + G$ and (c) the system $A + 2B \leftrightarrow C + D$ and $A + 2E \leftrightarrow F + G$. At the end of the contact time.

Near the reaction zone component B is regenerated by component E from the reaction products C and D with the simultaneous production of the other reaction products F and G. This regeneration of B reduces its diffusion limitation from the liquid bulk to the interface and therefore an essentially higher concentration of B is present near the interface and therefore the overall enhancement factor will be increased. In Fig. 6 the concentration profiles for an other case are presented. In this figure can be seen that the concentration of B is locally even greater than the liquid bulk concentration which implies that the production of B according to eq. (64) exceeds the transport to the bulk by means of molecular diffusion. This behaviour is due to similar phenomenon as forced desorption during simultaneous absorption of two gases onto a reactive liquid.

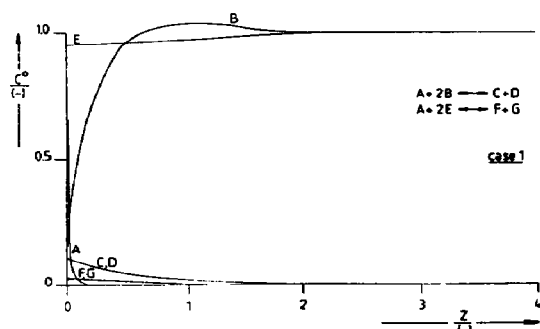
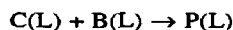


Figure 6: Dimensionless concentration profiles for the system $A + 2B \leftrightarrow C + D$ and $A + 2E \leftrightarrow F + G$. At the end of the contact time.

2.6. Absorption accompanied by consecutive reactions.

This group of processes can be divided in processes with two different forms of consecutive reactions:



Brian and Beaverstock (1965) studied the processes for group 1 numerically for both film model and penetration theory. However, their study was restricted to second order bi-molecular irreversible reactions. From their results it was concluded that the enhancement factor, as function of Φ_A , went through a maximum depending on the lifetime of intermediate product C. Ramachandran (1972) presented an overview of the processes of group 1 and presented analytical solutions for asymptotic cases. Bhattacharya and Ramachandran (1982) presented an analytically derived relation in case the rates of both reactions are instantaneously fast. This explicit relation is a function of the diffusivities, equilibrium constants and the bulk concentrations of B and P.

More attention has been paid to the consecutive reactions of group 2 and van de Vusse (1966a, 1966b) was the first who dealt with these processes. Approximate solutions for general irreversible kinetics were presented by, Teramoto et al. (1969), Onda et al. (1970c), Pangarkar and Sharma (1974a), and Kastánek and Fialová (1982). Only Huang et al. (1980) presented a numerical absorption model, however, only applicable to irreversible reactions.

It can be concluded that absorption processes accompanied by consecutive reactions have not been studied extensively, especially processes with reversible reactions.

2.7. Absorption accompanied by complex reactions.

In this section absorption processes will be treated which could so far not be classified.

Absorption processes with an irreversible autocatalytic reaction were numerically studied by Sim and Mann (1975) for the film model and by Joosten et al. (1980) for the penetration model.

The occurrence of a volatile liquid phase reactant is another phenomenon that has been studied. For the film model Pangarkar (1974) derived an approximate solution for the enhancement factor for an absorption process with a fast or instantaneous second order irreversible reaction regime. Shaikh and Varma (1984) generalized the work of Pangarkar so that no restrictions are imposed on the reaction regime. Ozturk and Shah (1986) developed an approximate solution for the penetration theory.

Kuo and Huang (1973) studied the simultaneous gas absorption and consecutive reversible chemical reactions for the film model and derived approximate solutions for some asymptotic situations. Gas absorption accompanied by an exotic system of reversible first-order reactions was investigated by Chu (1971). Owing to the fact that Chu only applied first order reactions he was able to derive analytical solutions.

3. DISCUSSION

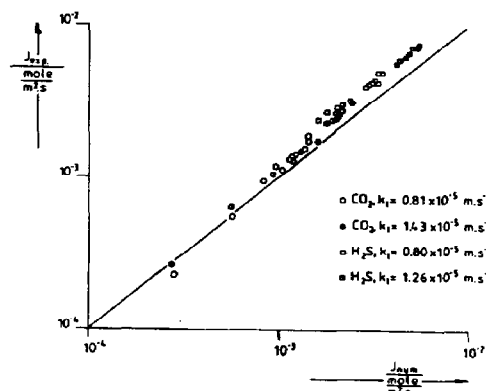


Figure 8: Comparison between measured and calculated absorption rates of H_2S and CO_2 in an aqueous monethanolamine solution at 298 K.

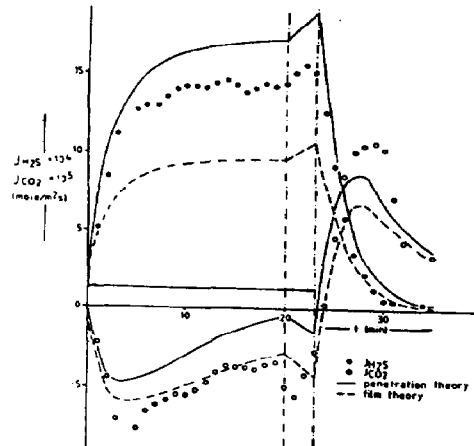


Figure 7: Measured and calculated H_2S and CO_2 molar fluxes during forced desorption conditions.

It is clear that the presented overview is not exhaustive and that the previously mentioned studies have in common an absorption process accompanied with chemical reactions for general applicable situations or reaction kinetics. Besides these studies large amounts of information have been presented on the description of absorption phenomena for dedicated processes, see e.g., Gioia and Astarita (1965), Pangarkar and Sharma (1974b), Astarita and Savage (1982), Al-Ghawas and Sandall (1988), Glasscock and Rochelle (1989), Bosch et al. (1989b) and Littel et al. (1991). Generally, it can be concluded that with the aid of dedicated and detailed absorption models the behaviour of physical and chemical properties of processes could be determined and make useful for practical applications.

The applicability of the absorption models, both approximate and numerically solved, is determined by the reliability of the simulations compared to the outcome of experiments. Blauwhoff

and van Swaaij (1985) verified experimentally the phenomenon forced desorption and Versteeg et al. (1989 and 1990) validated systematically absorption processes with complex reversible and reversible parallel reactions. Some of the results are presented in Fig. 7-10. Overall it can be concluded that the absorption models are satisfactory accurate for engineering purposes to estimate rates for chemical absorption processes if the physico-chemical data are known.

In point of view of the results of the experimental validation it can be concluded that for accuracy reasons further refinements are not necessary. Glasscock and Rochelle (1989) implemented the Nernst-Planck equations for diffusion and reaction in ionic systems in order to assure overall electroneutrality in the liquid phase. Littel et al. (1991) studied systematically the influence of ionic species on the absorption rates. From the simulation results they concluded that, compared to the absorption models in which electroneutrality was assured by means of equal diffusivities of the ionic species, the deviation was negligible for practical process conditions. Therefore it seems not necessary from point of view of accuracy to refine the description of the absorption processes by means of e.g., multi-component diffusion (e.g., Delancey, 1974 and Vanni and Baldi, 1991).

Only to the aspect of absorption processes with large exothermic effects little attention has been paid to. Recently, Bhattacharya et al. (1987, 1988a,b) presented some studies on gas absorption with exothermic effects. With the increasing popularity of the reactive (kinetic) distillation processes this phenomenon may turn out to be of some importance in the near future.

Therefore it must be concluded that the attention should be paid to the acquisition of the physico-chemical parameters and to the description of interfacial turbulence effects (e.g., Marangoni). The latter aspect possibly may be implemented in the mass transfer models by means of e.g., eddy diffusivity (King, 1966).

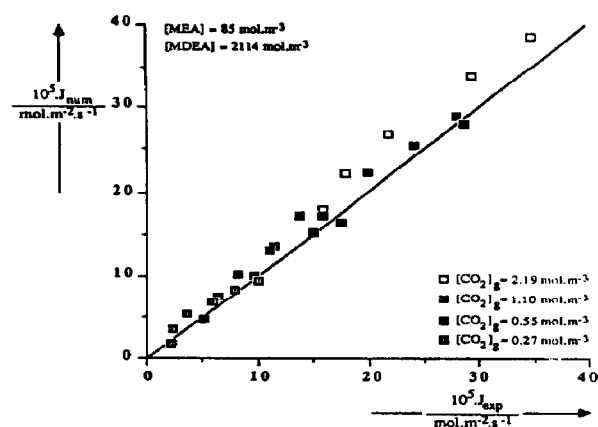


Figure 9: Comparison between measured and calculated absorption rates of CO_2 in an aqueous mixture of monethanolamine and methyl-diethanolamine at 298 K.

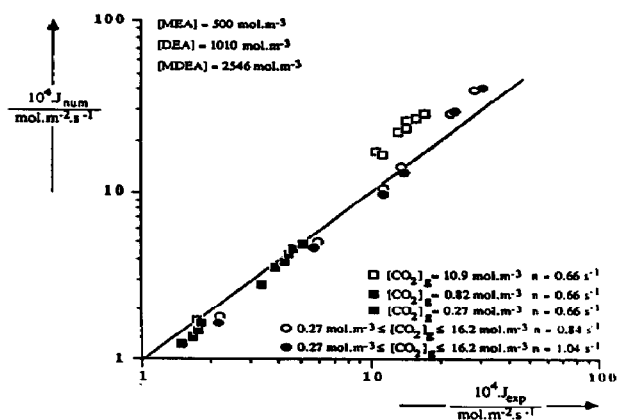


Figure 10: Comparison between measured and calculated absorption rates of CO_2 in an aqueous mixture of monethanolamine, diethanolamine and methyl-diethanolamine at 298 K.

4. CONCLUSIONS.

Because of the rapid development of the computational speed and capacity of the computers in combination with the availability of sophisticated mathematical software packages, no longer any limitation exists on rigorously numerically solving of dedicated and detailed absorption models for very complex absorption process. Therefore it must be concluded that it is of very little practical and industrial importance to develop approximate solutions and methods for these processes. The only application could be for educational purposes.

Finally it must be emphasized that the applicability and the reliability of absorption models is completely determined by the availability of the physico-chemical data that are required as input parameters. Therefore it must be concluded that the study and description of absorption processes, the determination of kinetic, thermodynamic, hydrodynamic and physical constants still is very important research item.

NOTATION

A	component A.
B	component B.
C	component C or concentration.
D	component D.
$D_{\text{subscript}}$	diffusivity, $\text{m}^2.\text{s}^{-1}$.
E	component E.

subscripts.

a	component A.
an	analytical solution.
b	component B.
c	component C.
d	component D.

$E_{\text{subscript}}$	enhancement factor, -.	e	equilibrium.
$E_{\text{subscript},\infty}$	infinite enhancement factor, -.	G	gas phase.
F	component F.	i	interface or species i.
G	gas phase.	L	liquid phase
J	mol flux, $\text{mol.m}^{-2}.\text{s}^{-1}$.	m	maximum value.
K	equilibrium constant	m	number indication of place
k_G	gas-phase mass transfer coefficient, m.s^{-1} .		step in discretization scheme.
k_L	liquid-phase mass transfer coefficient, m.s^{-1} .	num	numerical solution.
$k_{\text{subscript}}$	reaction rate constant, $m^3(m+n+p+q-1)_{\text{mol}}(m+n+p+q-1)_{\text{s}^{-1}}$ or $m^3(r+s+t+v-1)_{\text{mol}}(r+s+t+v-1)_{\text{s}^{-1}}$.	0	concentration at bulk conditions.
m	reaction order, -.	total	total
m_i	dimensionless solubility defined as $C_{A,L}/C_{A,G}$, l.		
q	reaction order, -.	L	liquid phase.
r	place variable after transformation defined by Eqn. (51)	p	reaction order, -.
s	reaction order, -.	n	reaction order, -.
t	reaction order, -.	R_i	reaction rate, $\text{mol.m}^{-3}.\text{s}^{-1}$.
ϕ_A	Ha-number defined by $(k_{m,n,p,q}C_{A,L}^{m-1}C_{B,L}^nC_{C,L}^pC_{D,L}^qD_A)/k_L$, -.	r	reaction order, -.
δ	film thickness according to the film model, m.	t	time variable, s.
θ	contact time according to the penetration model, s.	v	reaction order, -.
		α	solute loading defined by $C_{A,L,\text{total}}/C_{B,L,\text{total}}$, -.

References

- Al-Ghawas, H.A. and O.C. Sandall, (1988), Modelling of the simultaneous transport of two acid gases in tertiary-amines with reversible reactions, *Sep. Sci. and Technology*, **23**, 1523-1540.
- Alper, E., (1972), Absorption of a gas into a solution containing two reactants, *Chem. Engng Sci.*, **27**, 649-650.
- Alper, E., (1973), Absorption of a gas into a solution containing more than one reactant: analytical solution for instantaneous reactions, *Chem. Engng Sci.*, **28**, 1499-1500.
- Astarita, G. and F. Gioia, (1965), Simultaneous absorption of hydrogen sulfide and carbon dioxide in aqueous hydroxide solutions, *Ind. Engng. Chem. Fund.*, **4**, 317-320.
- Astarita, G. and D.W. Savage, (1982), Simultaneous absorption with reversible instantaneous chemical reaction, *Chem. Engng. Sci.*, **37**, 677-686.
- Baker, G.A. and T.A. Oliphant, (1960), An implicit method for solving the two-dimensional heat equation, *Quart. Appl. Math.*, **17**, 361-373.
- Barreto, G.F. and I.H. Farino, (1982), An approximate solution to the simultaneous chemical absorption of two gases, one gas reacts instantaneously, *Chem. Engng. J.*, **24**, 81-87.
- Bhattacharya, A. and P.A. Ramachandran, (1982), Analysis of gas absorption with a two-step instantaneous reversible reactions, *Chem. Engng. J.*, **25**, 215-218.
- Bhattacharya, A., Gholap, R.V. and R.V. Chaudhari, (1987), Gas absorption with exothermic bimolecular (1,1 order), *AIChE J.*, **33**, 1507-1513.
- Bhattacharya, A., Gholap, R.V. and R.V. Chaudhari, (1988a), An analysis of gas-absorption accompanied by an exothermic consecutive reaction, *Chem. Engng. Sci.*, **43**, 2890-2893.
- Bhattacharya, A., Gholap, R.V. and R.V. Chaudhari, (1988b), Gas absorption with exothermic bimolecular reaction in a thin liquid film: fast reactions, *Can. J. Chem. Engng.*, **66**, 599-604.
- Blauwhoff, P.M.M. and W.P.M. van Swaaij, (1985), Simultaneous mass transfer of H_2S and CO_2 with complex chemical reactions in an aqueous diisopropanolamine solution, *Chem. Engng. Proc.*, **19**, 67-83.
- Brian, P.L.T., Hurley, J.F. and E.H. Hasseltine, (1961), Penetration Theory for Gas Absorption accompanied by a second order chemical reaction, *AIChE J.*, **7**, 226 -231.
- Brian, P.L.T. and M.C. Beaverstock, (1965), Gas absorption accompanied by a two step chemical reaction, *Chem. Engng. Sci.*, **20**, 47-56.
- Bosch, H., Kuipers, J.A.M., van Swaaij, W.P.M. and G.F. Versteeg, (1989a), Mass Transfer with Complex Chemical Reactions. Simultaneous Absorption of H_2S and CO_2 in solutions of Alkanolamines, *Gas Separation & Purification*, **3**, 75-84.
- Bosch, H., Versteeg, G.F. and W.P.M. van Swaaij, (1989b), Gas-Liquid Mass Transfer with Parallel Reversible Reactions -I. Absorption of CO_2 into Solutions of Sterically Hindered Amines, *Chem.Engng.Sci.*, **44**, 2295-2310.
- Chang, C.S. and G.T. Rochelle, (1982), Mass Transfer enhanced by equilibrium reactions, *Ind. Engng. Chem. Fund.*, **21**, 379-385.
- Chu, C., (1971), Gas Absorption accompanied by a system of first-order reactions, *Chem.Engng.Sci.*, **26**, 305-312.
- Cornelisse, R., Beenackers, A.A.C.M. and W.P.M. van Swaaij, (1977), Simultaneous absorption of two gases in a reactive liquid, one gas reacting instantaneously, *Chem. Engng. Sci.*, **32**, 1532-1535.
- Cornelisse, R., Beenackers, A.A.C.M., van Beckum, F.P.H. and W.P.M. van Swaaij, (1980), Numerical calculation of simultaneous mass transfer of two gases accompanied by complex reversible reactions, *Chem. Engng. Sci.*, **35**,

1245-1260.

- Danckwerts, P.V., (1951), Significance of liquid-film coefficients in gas absorption, *Ind. Engng.Chem.*, **43**, 1460-1467.
- Danckwerts, P.V., (1970), *Gas-Liquid Reactions*, McGraw-Hill.
- DeCoursey, W.J., (1974), Absorption with chemical reaction. Development of a new relation for Danckwerts model, *Chem. Engng. Sci.*, **29**, 1867-1872.
- DeCoursey, W.J., (1982), Enhancement factors for gas absorption with reversible reaction, *Chem. Engng. Sci.*, **37**, 1483-1489.
- DeCoursey, W.J. and R.W. Thring, (1989), Effects of unequal diffusivities on enhancement factors for reversible and irreversible reaction, *Chem. Engng. Sci.*, **44**, 1715-1721.
- Delancey, G.B., (1974), Multicomponent film-penetration theory with linearized kinetics. 1. Linearization theory and flux expressions, *Chem. Engng. Sci.*, **29**, 2315-2323.
- Dobbins, W.E., (1956), *Biological Treatment of Sewage and Industrial Wastes*, McCable, M.L. and W.W. Eckenfelder(eds.) Part 2-1, Reinhold, New York.
- Edgerton, M.E., Byrne, G.D. and W.S. Ho, (1986), Numerical calculation of the simultaneous absorption of two gases with reversible chemical reactions, *Comp. & Chem. Engng.*, **10**, 551-556.
- Glasscock, D.A. and G.T. Rochelle, (1989), Numerical Simulation of theories for gas-absorption with chemical reaction, *AIChE J.*, **35**, 1271-1281.
- Goetler, L.A. and R.L. Pigford, (1971), Computational studies of the simultaneous chemical absorption by complex reaction, *AIChE J.*, **17**, 793-800.
- Hatta, S., (1932), *Tech. Repts. Tohoku Imp. Univ.*, **10**, 119
- Higbie, R., (1935), The rate of absorption of a pure gas into a still liquid during short periods of exposure, *Trans. Am. Inst. Chem. Engrs.*, **35**, 36-60.
- Hikita, H. and S. Asai, (1963), Gas Absorption with (m,n)-th-order Irreversible Chemical Reaction, *Kagaku Kogaku*, **11**, 823-830.
- Hikita, H. and S. Asai, (1964), Gas Absorption with (m,n)-th-order Irreversible Chemical Reaction, *Int. Chem. Engng*, **4**, 332-340.
- Hikita, H., Asai, S. and H. Ishikawa, (1977), Simultaneous absorption of two gases which react between themselves in a liquid, *Ind. Chem. Engng. Fund.*, **16**, 215-219.
- Hikita, H., Asai, S. and H. Ishikawa, (1979), Simultaneous absorption of two gases in a reactive liquid, one gas reacting instantaneously. *Chem. Engng. J.*, **18**, 169-172.
- Huang, C.-J. and C.-H. Kuo, (1965), Mathematical Models for Mass Transfer Accompanied by Reversible Chemical Reaction, *AIChE J.*, **11**, 901-910.
- Huang, D.T.J., Carberry, J.J. and A. Varma, (1980), Gas absorption with consecutive 2nd-order reactions, *AIChE J.*, **26**, 832-839.
- Jhaveri, A.S., (1969), Absorption of a gas into a solution containing two reactants, *Chem. Engng. Sci.*, **24**, 1738-1740.
- Joosten, G.E.H., Maatman, H., Prins, W. and E.J. Stamhuis, (1980), Gas absorption with autocatalytic reaction and simultaneous desorption of the catalyst, *Chem. Engng. Sci.*, **35**, 223-231.
- Karlsson, H.T. and I. Bjerle, (1980), A general explicit enhancement factor for irreversible gas-liquid reactions with gas-side resistance, *Chem. Engng. Sci.*, **35**, 1005-1007.
- Kastánek, F. and M. Fialová, (1982), Possible application of approximate models for calculation of selectivity of consecutive reactions under the effect of mass transfer, *Coll. Czech. Chem. Comm.*, **47**, 1301-1309.
- King, C.J., (1966), Tubulent liquid phase mass transfer at a free gas-liquid interface, *Ind. Engng. Chem. Fund.*, **5**, 1-8.
- van Krevelen, D.W. and P.J. Hoftijzer, (1948), Kinetics of Gas-Liquid Reactions. Part 1: General Theory, *Rec. Trav. Chim.*, **67**, 563-586.
- Kuo, C.H. and C.J. Huang, (1973), Simultaneous Gas Absorption and Consecutive Reversible Chemical Reactions, *Chem. Engng. J.*, **5**, 43-49.
- Li, K.Y., Kuo, C.H. and J.L. Weeks, (1974), Mass transfer accompanied by parallel reversible chemical reactions, *Can. J. Chem. Engng.*, **52**, 569-575.
- De Lind van Wijngaarden, G., Versteeg, G.F. and A.A.C.M. Beenackers, (1986), Mass-Transfer Enhancement Factors for Reversible Gas-Liquid Reactions: Comparison of DeCoursey's and Onda's, Methods, *Chem. Engng. Sci.*, **41**, 2442-2446.
- Littel, R.J., Filmer, B., Versteeg, G.F. and W.P.M. van Swaaij, (1991), Modelling of simultaneous absorption of H₂S and CO₂ in alkanolamine solutions: the influence of parallel and consecutive reversible reactions and the coupled diffusion of ionic species, *Chem. Engng. Sci.*, **46**, 2303-2313.
- Marek, M. and J. Schongut, (1979), Approximate relations for the calculation of enhancement factor in gas absorption with chemical reaction, *Coll. Czech. Chem. Comm.*, **44**, 475-487.
- Olander, D.R., (1960), Simultaneous Mass Transfer and Equilibrium Chemical Reaction, *AIChE J.*, **6**, 233-239.
- Onda, K., Sada, E., Kobayashi, T. and M. Fujine, (1970a), Gas Absorption Accompanied with Complex Chemical Reactions - I. Reversible Chemical Reactions, *Chem. Engng. Sci.*, **25**, 753-760.
- Onda, K., Sada, E., Kobayashi, T. and Fujine, M., (1970b), Gas absorption accompanied by complex chemical Reactions - III: Parallel chemical reactions, *Chem. Engng. Sci.*, **25**, 1023-1031.
- Onda, K., Sada, E., Kobayashi, T. and M. Fujine, (1970c), Gas Absorption Accompanied with Complex Chemical Reactions - II. Consecutive Chemical Reactions, *Chem. Engng. Sci.*, **25**, 761-768.
- Onda, K., Sada, E., Kobayashi, T. and M. Fujine, (1972), Gas Absorption Accompanied by Complex Chemical

- Reactions - IV. Unsteady State, *Chem. Engng. Sci.*, **27**, 247-255.
- Ozturk, S.S. and Y.T. Shah, (1986), Gas absorption with chemical reaction involving a volatile liquid reactant: penetration theory solution, *Chem. Engng. Commun.*, **46**, 65-71.
- Pangarkar, V.G. and M.M. Sharma, (1974a), Consecutive reactions, role of mass transfer factors, *Chem. Engng. Sci.*, **29**, 561-569.
- Pangarkar, V.G. and M.M. Sharma, (1974b), Simultaneous absorption and reaction of two gases. Absorption of CO₂ and NH₃ in water and aqueous solutions of alkanolamines, *Chem. Engng. Sci.*, **29**, 2297-2306.
- Pangarkar, V.G., (1974), Gas absorption with reaction in a solution containing a volatile reactant, *Chem. Engng. Sci.*, **29**, 877-882.
- Patwardhan, V.S., (1981), Enhancement factor in gas-liquid reactions in presence of significant gas side mass transfer resistance for a 2nd-order reaction, *Chem. Engng. Sci.*, **36**, 222-224.
- Perry, R.H. and R.L. Pigford, (1953), Kinetics of Gas-Liquid Reactions. Simultaneous Absorption and Chemical Reaction, *Ind. Engng. Chem.*, **45**, 1247-1253.
- Porter, K.E., Cantwell, A.D.C., and C. McDermott, (1971), Absorption and desorption accompanied by a reversible reaction, *AIChE J.*, **17**, 536-541.
- Ramachandran, P.A. and M.M. Sharma, (1971), Simultaneous absorption of two gases, *Trans. Inst. Chem. Engng.*, **49**, 253-280.
- Ramachandran, P.A., (1972), Mass transfer accompanied by two step chemical reaction, *Chem. Engng. Sci.*, **27**, 1807-1816.
- Roper, G.H., Hatch, T.I. and R.L. Pigford, (1962), Theory of absorption and reaction of two gases in a liquid, *Ind. Engng. Chem. Fund.*, **1**, 144-152.
- de Santiago, M. and I.H. Farina, (1970), Mass transfer with second order reaction. Numerical solution, *Chem. Engng. Sci.*, **25**, 744-747.
- Secor, R.M. and J.A. Beutler, (1967), Penetration Theory for Diffusion Accompanied by a Reversible Chemical Reaction with Generalized Kinetics, *AIChE J.*, **13**, 365-373.
- Shaikh, A.A. and A. Varma, (1984), Gas absorption with chemical reactions. The case involving a volatile liquid component, *Chem. Engng. Sci.*, **39**, 1639-1641.
- Sim, M.T. and R. Mann, (1975), Gas absorption with autocatalytic reaction, *Chem. Engng. Sci.*, **30**, 1215-1218.
- Teramoto, M., Nagayasu, T., Matsui, T., Hashimoto, K. and S. Nagata, (1969), *Selectivity of Consecutive Gas-Liquid Reactions*, J.Chem. Engng. Jpn., **2**, 186.
- Toor, H.L. and J.M. Marchello, (1958), Film-Penetration model for mass transfer and heat transfer, *AIChE J.*, **4**, 97-101.
- Vanni, M. and G. Baldi, (1991), Mass transfer and chemical reaction with multi-component diffusion, *Chem. Engng. Sci.*, **46**, 2465-2472.
- Versteeg, G.F., Kuipers, J.A.M., van Beckum, F.P.H. and W.P.M. van Swaaij, (1989), Mass Transfer with Complex Reversible Chemical Reactions- I. Single Reversible Chemical Reactions, *Chem. Engng. Sci.*, **44**, 2295-2310.
- Versteeg, G.F., Kuipers, J.A.M., van Beckum, F.P.H. and W.P.M. van Swaaij, (1990), Mass Transfer with Complex Reversible Chemical Reactions- II. Parallel Reversible Chemical Reactions, *Chem. Engng. Sci.*, **45**, 183-197.
- van de Vusse, J.G., (1966a), Consecutive reactions in heterogeneous systems. 1. The effect of mass transfer on selectivity, *Chem. Engng. Sci.*, **21**, 631-643.
- van de Vusse, J.G., (1966b), Consecutive reactions in heterogeneous systems. 2. Influence of order of reaction rates on selectivity, *Chem. Engng. Sci.*, **21**, 645-654.
- Wellek, R.M., Brunson, R.J. and F.H. Law, (1978), Enhancement factors for gas absorption with 2nd-order irreversible chemical reaction, *Can. J. Chem. Engng.*, **56**, 181-186.
- Whitman, W.G., (1923), Preliminary experimental confirmation of the two-film theory of gas absorption, *Chem&Met. Engng.*, **29**, 146-148.
- Winkelman, J.G.M., Brodsky, S.J. and A.A.C.M. Beenackers, (1992), Effects of unequal diffusivities on enhancement factors for reversible reactions: numerical solutions and comparison with DeCoursey's method, *Chem. Engng. Sci.*, **47**, 485-489.
- Yeremia, A.A., Gottifredi, J.C. and J.J. Ronco, (1970), Mass Transfer with homogeneous second order irreversible reaction. A note on an explicit expression for the reaction factor, *Chem. Engng. Sci.*, **25**, 1622-1624.
- Zaryckzi, R., Ledakowicz, S. and M. Starzak, (1981), Simultaneous absorption of two gases reacting between themselves in a liquid. 2. Approximate solutions, *Chem. Engng. Sci.*, **36**, 113-121.